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TECHNOLOGICAL ASPECTS OF USE OF RAW MATERIALS IN THE GLASS INDUSTRY

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Further increasing the efficiency of glass making is a function of improving the homogeneity of the batch used. For obtaining a homogeneous batch and preventing it from separating, it is necessary to calculate the optimum mixing time for each type of mixer.

The Russian glass industry has entered a new stage of development. This stage is characterized by the following:

a sharp increase in the rate of development and production volumes of sheet and container glass (10 – 12% increase);

expansion of the assortment of articles made from sheet and container glass;

a marked increase in investments in the sector;

an increase in the technical level due to restoration of basic resources;

intensification of competition among glass manufacturers;

stiffening of requirements for the quality and assortment of articles by consumers of glass;

the appearance of problems related to the raw-material base of the glass industry.

We will basically discuss the last point, but since the raw-material problem derives from the factors given in the preceding paragraphs, we will briefly analyze them.

The growth in the rate of development of the glass-container industry is due to the evolution of beverage manufacture. In the last 5 – 6 years, beverage manufacture increased from 10 – 12 liters (including 6 liters for beer) per capita to 80 – 100 liters (including 50 liters for beer). Bottle manufacture increased from 1.2 billion units in 1990 to 11.5 billion units in 2005. In addition, the assortment of glass-container products also expanded. Large glass-container factories manufacture up to 8 – 10 types of bottles. It is thus difficult to organize recycling of used containers. Reuse of glass containers is held back even more because of the expensive, difficult to remove detergents used to prepare them. Finally, the cost of glass breakage is totally comparable to the cost of a "recycled" bottle.

As for sheet glass, it should be noted that a powerful subsector of the glass industry has recently arisen – industrial processing of glass with production of double glass panes, energy-saving glass (glass with low-emission coatings), safe, fire-resistant, self-cleaning glass. In the last two years, the volume of construction increased by 11.5 – 12.5%. Production of sheet glass also increased commensurately. On the whole, the demand exceeds 150 million m^2 a year.

In conditions of a significant increase in production volumes and expansion of product lines, the competition between manufacturers and consumer quality requirements have increased.

This objective process was responded to by the industry – its technical level increased significantly primarily due to renovation and modernization of basic resources. According to our estimations, up to 85% of sheet glass, the products of processing it, and container glass is manufactured on equipment 15 years old and younger. This involves tens of measuring-mixing lines that ensure measuring accuracy no worse than 0.2% of the highest measuring limit, glass-making furnaces that ensure removal of a minimum of 2000 – 3000 kg/m^2 from the melting part of the furnace and specific heat consumption of 950 – 1400 kcal/kg of glass melt, imported machine lines for molding glass containers and sheet glass, and lines for industrial glass processing.

The resources in optimizing equipment designs and operating conditions have been exhausted to a significant degree. Further increasing the efficiency of operation of glass works is correlated with improving the homogeneity of the raw materials and mixtures of raw materials (batches).

Batch quality is a statistical quantity and is a function of the accuracy of calculating the batch formula, the stability of the chemical composition of the raw materials, the accuracy of its analysis, the accuracy of measuring, and the quality of mixing. The mathematical model correlating the composition of the batch and raw material in vector-matrix form is as follows [1]:

$$Y = AX, \tag{1}$$

where Y is the n-dimensional vector of the chemical composition of the batch; A is the matrix of raw material nm; X is the m-dimensional vector of the weight of the raw material.

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TABLE 1

Factory	Absolute value of different contributions,* 10^{-6}, in batch quality analysis									
	Variations in composition of raw material						Sum of contributions of variations in raw material composition	Batching error	Error of calculating formula	Criterion *SpR*, 10^{-6}
	sand	feldspar, pegmatite	dolomite	limestone	soda	sodium sulfate				
Saratov	0.63	0.01	1.04	3.33	0.1	0	5.11	1.03	0.06	6.20
	(10.15)	(0.20)	(16.70)	(53.60)	(1.67)	(0)	(82.36)	(16.60)	(1.09)	(100)
Bor	0.58	0.10	0.79	0.09	0.79	0	2.30	1.97	0.03	4.3
	(3.58)	(2.25)	(18.48)	(0.99)	(18.43)	(0)	(53.74)	(45.98)	(0.36)	(100)
Kirish	1.87	1.05	1.00	0.93	0.52	0.04	5.51	1.05	0.12	6.68
	(34.60)	(19.40)	(18.20)	(17.00)	(9.60)	(0.70)	(82.50)	(15.70)	(0.18)	(100)
Orekhovo-Zuevo	3.45	0.08	2.41	0	0.12	1.07	7.13	1.04	0.12	8.29
	(48.40)	(1.10)	(33.80)	(0)	(1.60)	(15.10)	(86.00)	(12.60)	(1.40)	(100)
Salavat:										
new DSL	0.65	0.01	1.08	2.01	0.10	0	3.85	0.8	0.17	4.82
	(16.88)	(0.26)	(28.05)	(52.21)	(2.60)	(0)	(79.90)	(16.60)	(3.50)	(100)
old DSL	0.68	0.01	1.02	1.98	0.10	0	3.79	3.1	0.05	6.94
	(17.92)	(0.26)	(26.90)	(52.27)	(2.70)	(2.70)	(54.60)	(44.70)	(0.70)	(100)

* The value of the contribution of each factor, %, is given in parentheses.

A rigorous solution of Eq. (1) is only possible in the case of a square matrix A, i.e., if the number of components of the raw material (oxides) and the number of components of the batch (raw materials) coincide. In the other cases, several approximate solutions which occur in practice in operation of glass works in calculation of the batch formula are found. The batch quality can be assessed quantitatively with a matrix of variation of the oxide content in the batch R – the multidimensional analog of dispersion [2, 3]:

$$R = M\{(AX - \overline{Y})(AX - \overline{Y})^{\mathrm{T}}\}; \quad (2)$$

$$R = (\overline{A}\,\overline{Y} - \overline{Y})(\overline{A}\,\overline{X} - \overline{Y})^{\mathrm{T}} + A\Psi_x A^{\mathrm{T}} + \Sigma(\overline{x}_{\mu}^2 + \sigma_{x\mu}^2)\,\Psi_x;$$

$$spR = \mathrm{II}\overline{A}\,\overline{X} - \overline{Y}\,\mathrm{II}^2 + \overline{X}^{\mathrm{T}} D\overline{X} + sp\,(\overline{A}\Psi_x \overline{A}^{\mathrm{T}}) + sp\,(D\Psi_x), \quad (3)$$

where A is the nm matrix of average raw material composition; M is the mathematical expectation; T is the matrix transposition sign; Ψ_x is the covariation matrix of batching errors; x_{μ} is the weight of the μth component of the batch (raw material); D is the batch composition scatter matrix; $\sigma_{x\mu}$ is the variance of the weight (i.e., of one component in one weighing); SpR is the trace of matrix R.

The physical meaning of Eq. (3) is as follows:

the first term characterizes the error that arises in calculating the formula of the batch due to ambiguous solution of (1); the error appears when the number of components of the glass (oxides) does not agree with the number of raw material components of the batch; in addition, there are restrictions: $y_i > 0$ (nonnegative solution), $\Sigma x_i = 1$, soda-sulfate ratio;

the second term is an estimation of the error of the chemical composition of the batch that arises due to variation of the composition of the raw material, and the error of the method of taking samples and their chemical analysis;

the third and fourth terms estimate the contribution of the errors of measuring out the raw material.

Data from analyzing the batch quality based on criterion *SpR* for five glass works are reported in Table 1, and the contribution of variations in the oxide content in the raw materials (homogeneity of the raw material), of the errors of the batching error and the errors of calculating the batch formula to the error of the batch composition.

The error was estimated with the *SpR* criterion, i.e., the sum of variances of the contributions of the listed process factors to the quality of the glass batch. Variations of the oxide content in the raw materials were determined as the scattering average over 6 months in almost daily measurements. A file of several hundred measurements in operating the batchers – random sampling over 6 months – was selected for estimating the variation in batching. The error of the analysis was the error of the method of analyses developed by the Glass Institute (Moscow). The error of calculating the batch formulation was determined by calculating the formulation with several methods from the Glass Institute, Stromizmeritel', etc.

It follows form the data in Table 1 that inhomogeneity of the raw materials makes the greatest contribution to inhomogeneity of the batch.

It is also important to compare the results of replacing aging DSL equipment from Transporta Co. (Czechoslovakia) with modern lines with batchers from Stromizmeritel' Co. and mixers from Orlovo Steklomash Factory. In the case of replacement, the contribution of variation of batching and errors of calculating the batch formula decreased sharply. Calculation of the formula was converted from "manual" to automated as the Stromizmeritel' Co. algorithm which optimized the batch formula was perfected.

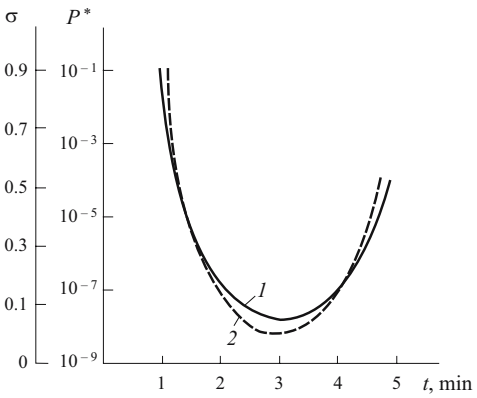

Fig. 1. Curve of mixing batch components in a mixer (*1*) and theoretical curve (*2*): σ – standard deviation, calculated with data from analysis with Eq. (2) for a concrete mixer.

Due to the multidimensionality of the matrix (*nn*, i.e., for a 7-component batch of 49 elements), A. E. Sorkina proposed using matrix trace *SpR*, i.e., the sum of diagonal elements, which is the sum of scattering of the variations in the content of the chemical components of the batch [4].

In factory laboratory conditions, the content of soda and sulfate, insoluble components, and sometimes carbonates were measured in rapid analysis of the batch.

The degree of inhomogeneity in factory practice is characterized not by vector-matrix, but by its simplified analog, scalar quantity – the standard deviation:

$$\sigma = \sqrt{\frac{n\sum_{i=1}^{n}(x_i - \bar{x})^2 g_i}{(n-1)\sum_{i=1}^{n} g_i}}.$$

The mechanism for blending the raw materials consists of increasing the interface between regions of inhomogeneity. This surface will be minimal in loading into the hopper, silo, or mixer by layers.

The intensity of the processes in the glass-making furnace is due to the development of the interface, since the rate of chemical reactions and diffusion and consequently fuel consumption are dependent on it. The increase in the interface, as E. I. Smirnov and I. B. Shlain showed, is proportional to the initial inhomogeneity:

$$\sigma = \sigma_o e^{-pt},$$

where σ_o is the standard deviation before blending; p is a coefficient that is dependent on the blending method; t is the time.

The methods of homogenizing bulk substances are divided into mixing – homogenization of a mixture of several components; blending – homogenization of one raw material or finished mixture; separation – removal of one or more components from a material (usually iron and aluminum oxides from sand). There are many methods of separation based on magnetic properties, differences in density or size, flotation, and attrition.

In addition to the fine methods based on a physical or physicochemical effect on the material, there are also methods of "coarse" blending.

Let us consider some questions in the theory of blending of materials.

The homogeneity of a mixture of raw material components (batch) can be defined as the presence of a composition corresponding to the formula of the batch in a minimal space. If this space is a so-called closely packed structure (tetrahedron, cube, octahedron, dodecahedron, icosahedron), the tendency of the batch to separate will be minimal. This should be the goal in selecting the granulometric composition of the raw material. The average grain radius of a component can be determined as follows:

$$r_i = r_j \sqrt[3]{\frac{p_i n_j k_j \rho_j}{p_j n_i k_i \rho_i}}, \qquad (4)$$

where p_i and p_j are the mass of the ith and jth components; n_i and n_j is the number of grains (particles); k_i and k_j are coefficients that account for deviation of the grain shape from spherical; ρ_i and ρ_j are the density ($i = 1, ..., n$; $j = 1, ..., n$).

The largest-grain component from the condition of optimizing the silicate- and glass-formation regime is dolomite (the optimum grain diameter is 1 – 3 mm). It is in the center of the closely packed cell. The granulometric composition of the other components can be selected with Eq. (4).

The mixing mode is theoretically selected as the maximum probability that particles of other components (with a radius determined with Eq. (4) and in a ratio corresponding to the formula of the batch) will fall on the surface of the dolomite grain. The curve shown in Fig. 1 is also coincides with the curve plotted with the experimental data.

The probability that no granule will fall on the surface of a large particle is:

$$P^*\left(\frac{r}{2},\ t\right) = \prod_{i=1}^{n} P_i\left(\frac{r_i}{2},\ t\right),$$

where r is the radius of the particle; t is the mixing time; $i = 1, ..., n$ is the raw component index.

Several conclusions follow from the calculated and experimental data in Fig. 1: mixing and separation are "mirror-image" processes; the blended mixture separates on further activation; for this type of mixer, the optimum mixing time varies between 2.5 – 4 min.

In continuous loading of raw material in the operating mixer, all of the components should be loaded in 1 – 1.5 min. Otherwise they will fall into the separation interval. Distinct synchronization of the measurement and mixing processes is thus required.

The next important conclusion deriving from the data in Fig. 1 is the presence of residual inhomogeneity of the mixture (material).

The standard deviation through k blending cycles can be represented as the sum:

$$\sigma_k = \sigma_0 e^{-p,k} + \sigma_{res}(1 - e^{-p,k}),$$

where σ_{res} is the residual, equilibrium inhomogeneity, which is a function of the type of mixer and mixing time.

Further increasing the efficiency of glass-making processes will thus be dependent on improving the homogeneity of the batch used. The optimum mixing time must be calculated for each type of mixer in order to obtain a homogeneous batch and prevent it from separating.

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